

UNIVERSITY OF PENNSYLVANIA

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OF MERCURY TO CHLORINE
IN MERCURIC CHLORIDE

CLAUDE K. DEISCHER

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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INTRODUCTION.

Prior to 1900, investigators obtained values for the atomic weight of mercury ranging from 199.677 to 200.626. Because of the lack of consistency in these results (and particularly where the same ratios were used) we may overlook these previous values.¹

Especially is this evident in the investigations and results of Turner,² Erdmann and Marchand,³ and Hardin.⁴

A careful examination of the investigations since 1900 shows the following ratios and the atomic weight of mercury obtained therefrom:

Easley, J. Am. Chem. Soc., **31**, 1207 (1909)—

$\text{HgCl}_2 : \text{Hg} = 200.48$; $\text{HgCl}_2 : 2\text{AgCl} = 200.62$.

Easley, J. Am. Chem. Soc., **32**, 1117 (1910)—

$\text{HgCl}_2 : \text{Hg} = 200.63$.

Easley and Braun, J. Am. Chem. Soc., **34**, 137 (1912)—

$\text{HgBr}_2 : 2\text{AgBr} = 200.64$.

Taylor and Hulett, J. Phys. Chem., **17**, 755 (1913)—

$\text{HgO} : \text{Hg} = 200.371$.

Baker and Watson, J. Chem. Soc., **105**, 2530 (1913)—

$\text{Hg} : 2\text{Br} = 200.578$.

Hönigschmid, Birckenbach and Steinheil, Ber. **56 B**, 1212 (1923)—

$\text{HgCl}_2 : 2\text{Ag} = 200.61$; $\text{HgBr}_2 : 2\text{Ag} = 200.61$.

Aston, Proc. Roy. Soc. (London), **A 126**, 511 (1928)—

Calculated from isotopes — 200.626.

From such examination, all investigations are found to be involved and hence require several intermediate steps to obtain the result. This necessitated a careful preparation of many reactants, as well as the application of corrections for difficulties en-

¹ Clarke, F. W., Mem. of the Nat. Acad. of Sci., 3d Mem., Vol. 16.

² Turner, E., Phil. Trans., 531 (1833).

³ Erdmann and Marchand, J. prakt. Chem., **31**, 395 (1844).

⁴ Hardin, W. L., J. Am. Chem. Soc., **18**, 1003 (1896).

countered. It is a well-known fact that the errors were increased by (1) the use of alkaline or ammoniacal reducing solutions which favored the introduction of silica, (2) the lengthy period of time required for such reduction, (3) the handling of large volumes of solution, or (4) the difficult removal of last traces of metal by electrolysis.

In view of these facts the author evolved a simplified method which it is believed will give greater accuracy. It is also hoped that the principles of this method may be employed, with slight variations, in the determination of the atomic weights of other elements. This method has the following distinguishing characteristics:

1. The use of a hitherto unused ratio, $\text{Hg} : 2\text{Cl}$.
2. The use of a specially constructed reaction vessel.
3. The entire reaction taking place in the same reaction vessel.
4. The elimination of involved quantitative methods of analysis.
5. The use of only one atomic weight of an element which has a well-determined value.

The average result obtained from ten experiments using this ratio gave 2.82781. This value recalculated as the atomic weight of mercury gave 200.532. Larger samples of mercury are used in work now in progress with the hope that the results will compare favorably with those already obtained.

EXPERIMENTAL.

A. PURIFICATION AND PREPARATION OF REAGENTS.

Mercury. The best mercury from two different reputable American companies was dropped through a tower similar to that constructed by Hildebrand,⁵ twenty (20) times and redistilled three times in a mercury still similarly constructed to that used by Hulett.⁶

Some of these samples were sealed in small ampoules under vacuum.

A few determinations made during the summer months varied so much that the mercury used and the products obtained were

⁵ Hildebrand, J. H., J. Am. Chem. Soc., **31**, 933 (1909).

⁶ Hulett, G. A., Phys. Rev., **33**, 307 (1911).

carefully examined. The tests will be fully described in detail in part D. A microscopic examination of the samples of mercury revealed small crystals of the oxide. These crystals were found in both the sealed samples (which stood for several months) and in freshly distilled mercury. The formation of oxide in sealed samples of mercury is a well known fact. The higher humidity of the air during the summer favors the formation of the oxide if it is drawn through the still during distillation. Hence the presence of oxide in freshly distilled samples.

To guard against the presence of the oxide, the later samples were dropped through a 5 per cent nitric acid solution in a miniature Pyrex glass tower similar to that used by Hildebrand. After repeating this operation ten times the resulting samples were washed five times with freshly distilled water and finally separated from the water by several extractions from small steamed oven dried Pyrex separating funnels. The samples were dried in a desiccator containing phosphorus pentoxide and used immediately.

A few samples of the prepared mercury were slowly volatilized in Sillimanite crucibles. These samples left no residue.

Water. The laboratory distilled water was redistilled from alkaline potassium permanganate and dilute sulphuric acid. The condenser was made of pure block tin, fitted to a Pyrex flask with a constricted neck. The water was collected in steamed Pyrex flasks and used immediately. The water only came in contact with the tin condenser and Pyrex glass.

Hydrochloric Acid. By treating concentrated hydrochloric acid with concentrated sulphuric acid (the best products of a reputable American manufacturer) the hydrogen chloride gas evolved was dried and dissolved in freshly distilled water until the solution had an approximate specific gravity of 1.06. Acid of such a concentration gave the best gentle evolution of chlorine with potassium permanganate.

Chlorine. The freshly prepared hydrochloric acid was dropped in a Pyrex glass generator containing the best recrystallized potassium permanganate.

Solid Carbon Dioxide. Commercial solid carbon dioxide was

used. It never was allowed to come in direct contact with the reaction vessel.

B. BALANCE AND WEIGHING.

All weighings were made on a Christian-Becker balance sensitive to 0.01 milligram with weights which had been carefully standardized according to the method used by Richards.⁷ The balance was placed in a large double-walled case with double glass panels and was operated entirely from the outside of this case by means of bakelite rods attached to each control of the balance.

Pyrex glass hook stands were used inside the balance to remove and replace the reaction vessel in order to determine the resting point of the empty balance. These hooks likewise helped to decrease the period of time required to obtain a constant weight. The average period of time was 50-80 hours, depending upon the atmospheric conditions at the time of transfer to the balance. Ordinary handling of the vessel with a lintless cloth and the hand destroyed the equilibrium between the vessel and the conditions inside of the balance. Therefore the period of time would be greatly increased with such handling.

The weight of the reaction vessel was always compared to a similarly treated counterpoise. The ground glass joints of the vessel were so turned that they were open to the balance atmosphere. This brought the vessel into equilibrium with conditions inside the balance much quicker. Electrostatic charges were eliminated by means of a small amount of radio-active salt placed in the balance case as well as a grounded condenser plate. Vacuum corrections were applied after noting the temperature, atmospheric pressure, and relative humidity inside the balance case after each weighing. Relative humidity measurements were made by means of a hair hygrometer. This was checked frequently against a sling psychrometer. The following densities were used:

Weights:

Brass	8.44	Pyrex glass	2.25
Platinum	21.2	Mercuric chloride	5.44
Aluminum Rider	2.65	Mercury ⁸ —varies with temperature.	

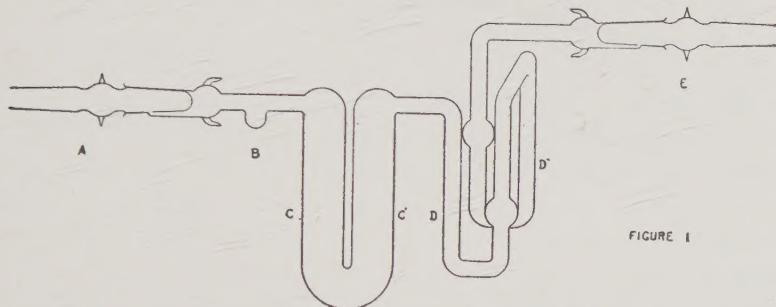
⁷ Richards, T. W., J. Am. Chem. Soc., **22**, 144 (1900).

⁸ Landolt-Bornstein, Phys. Chemische Tabellen — Seite 77, Edited by Roth and Scheel.

C. TREATMENT OF REACTION VESSEL.

The reaction vessel used, as shown in Fig. 1, was made of Pyrex glass and was of the same proportions except that the right arm, extending from the U tubes, was bent forward at a right angle so that the vessel could be placed on the hook of the balance pan without touching the side of the case. The vessel as shown in Fig. 1 was supported with a platinum wire while in the balance case. All joints were well ground and no lubricant was used at any time.

The vessels were thoroughly cleaned with cleaning solution, rinsed well with water and immersed for 15 minute periods in



3 separate portions of boiling freshly-distilled water. After steaming the vessels they were dried in an oven at $120^{\circ} C$. for several hours. The vessels were cooled in a large desiccator and later placed in the balance case with the ground joints so turned that they were open. This allowed the conditions inside of the reaction vessel to be the same as those in the balance case. After the usual period of time required for such an equilibrium the difference between the reaction vessel and the counterpoise was noted. The ground joint A was removed and mercury from a small drawn out Pyrex separating funnel was run into the bulb B. The ground joint was replaced, but so turned that it was open. Dry air was not drawn through the reaction vessel after the mercury had been placed in the bulb B because of the belief that a small amount of mercury might be carried by air into other parts of the reaction vessel which were not heated during the synthesis. This would ultimately produce mercurous chloride. That none of the mercury volatilized during the period required

for equilibrium of conditions inside and outside of the vessel is also evident by the tests made on the products. These tests are described in the following Division D. After determining the weight of the vessel with the mercury in equilibrium with the balance atmosphere it was ready to be connected to the system at the point indicated in Fig. 2.

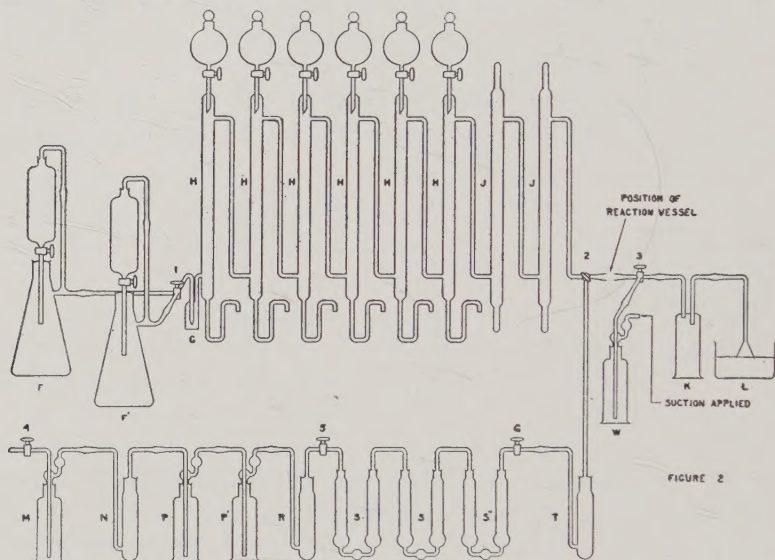


FIGURE 2

D. SYNTHESIS OF MERCURIC CHLORIDE.

After placing the reaction vessel containing the mercury in the system in the position indicated in Fig. 2, with both stopcocks 2 and 3 closed to either circuit, a small circular electric heater was placed around bulb B, Fig. 1. The U tubes D and D' in Fig. 1 were immersed in a small beaker which was placed in a larger crucible. At intervals solid carbon dioxide was packed between the crucible and the beaker. This caused the passing chlorine to liquefy, thus forming two traps. These served as an absorbent for any volatilized mercuric chloride which might be carried past C and C' in Fig. 1. None was ever detected in the second U tube D' after the chlorine was allowed to volatilize at the end of the experiment. Most of the chloride condensed in the tube C,

Fig. 1, because of the construction of the heater. The lower part of C and all parts of C' were at room temperature during the experiment.

The evolved chlorine, coming from either one or both of the chlorine generators F or F' in Fig. 2 was passed through a small bubbler, G, and six drying towers, H, filled with glass beads over which the best concentrated sulphuric acid flowed slowly. As a precaution, the dry gas was then passed through the two towers J containing glass wool to remove any sulphuric acid. The rate of evolution of the chlorine was such (approximately 50 bubbles per minute) that no acid ever collected in these towers. Stop-cocks 2 and 3 in Fig. 2 were so turned that the generated chlorine passed through the reaction vessel and any excess was dissolved in a cold concentrated sodium hydroxide solution in container L.

The heater surrounding bulb B, Fig. 1, was gradually raised to 265° C. and kept there until all the mercury had combined with the chlorine. That only mercuric chloride formed was evident on account of the large excess of chlorine passing through at all times as well as from solubility tests conducted with the products. The products were completely soluble in freshly distilled acetone and ether. The volume of solvent used was dependent upon the amount of product obtained. Had mercurous chloride been present it would have remained undissolved.⁹ Solutions of the products in distilled water were also tested with an excess of a freshly prepared solution of recrystallized potassium iodide and the resulting solutions were free of any residue. Moreover had mercurous chloride been present, free mercury would have separated after the addition of excess potassium iodide. Other samples were tested with ammonia water. Free mercury was absent. Therefore the samples were not contaminated with mercurous chloride.

The average of several melting point determinations of the product was 282.5° C. in closed capillary tubes. This proved the absence of mercurous chloride or any other foreign chlorides.

After the heater was disconnected chlorine was passed through this same circuit for an additional 30 minutes until the entire reaction vessel was at room temperature. The entire operation

⁹ Mellor, J. W., *Inorganic and Theoretical Chem.*, Vol IV, p. 818.

¹⁰ J. Am. Chem. Soc., **55**, 441 (1933).

required from six to eight hours depending on the amount of mercury used.

The chlorine generators were disconnected and later cleaned. The liquid chlorine in the U tubes (D and D', Fig. 1) was allowed to volatilize slowly and absorbed in the sodium hydroxide solution. Stopcocks 2 and 3, Fig. 2, were now turned so that both were open to the pure dry air inlet, yet including the reaction vessel in the circuit. After stopcocks 4, 5 and 6, Fig. 2, were opened, suction from a water pump was applied at the point indicated in Fig. 2. Sulphuric acid was kept in the drying bottle W, to prevent water vapor from getting into the reaction vessel containing the mercuric chloride. Air was drawn through the drying train consisting of a solution of acid permanganate in M, fused potassium hydroxide in N, concentrated sulphuric acid in P and P', glass wool in R, phosphorus pentoxide in S, S' and S'', glass wool in T, and finally through the reaction vessel to remove the chlorine by selective absorption. Air was drawn through the reaction vessel for two hours at the same rate as the chlorine was passed during the synthesis of the mercuric chloride.

Tests for free chlorine were made by passing the air, drawn from the reaction vessel containing the chloride, through acid-starch-potassium iodide solution in a vessel inserted between 3 and W, Fig. 2. No coloration was observed in any case after two hours passage.

To test the possibility that some mercuric chloride might be carried out of the reaction vessel containing the chloride, a few previously weighed vessels containing mercuric chloride were replaced in the system and air was drawn through for additional periods. The vessels were reweighed, showing no loss. The following are the results:

TABLE I.
Weight of Vessel + HgCl_2 After Air Treatment.

Time of Air Treatment	A	B
2 hours	0.49767	0.61639
4 hours	0.49767	
6 hours	0.49768	0.61640

Distilled water was added to weighed amounts of the product to yield approximately a 5.5 per cent solution. After adding o-tolidine the color of the solution was compared with standards and found to contain less than 0.1 part of free chlorine per million parts of solution. This result is identical with the result obtained with pure distilled water. Solutions of other samples were treated with recrystallized potassium iodide, starch solution, and a standard sodium thiosulphate solution, and all tests proved to be negative. After these tests it could be assumed that no free chlorine was present.

The reaction vessel was disconnected, washed on the outside with freshly distilled water and placed in a desiccator over phosphorus pentoxide until dry. Care was taken not to get any water in the ground joints. Before placing the vessel in the balance case, the outside of the vessel was cleaned with a camel's-hair brush. After the required period of time to attain equilibrium, the weight was noted and from the three weights, corrected to vacuum, the

TABLE II.

The Atomic Weight of Mercury.

Cl = 35.457

Hg: 2Cl

Experiment	Sample of Hg. used	Wt. of Hg. in Vac. in gms.	Wt. of $HgCl_2$ in Vac. in gms.	Wt. of Cl combined with Hg in Vac. in gms.	Ratio Hg: 2Cl	At. Wt. of Hg.
1	A-3 x dist.	0.64403	0.87177	0.22774	2.82791	200.538
2	A-3 x dist.	0.61153	0.82779	0.21626	2.82775	200.527
3	A-3 x dist.	0.65849	0.89135	0.23286	2.82783	200.533
4	B-3 x dist.	0.52408	0.70941	0.18533	2.82782	200.532
5	B-6 x dist.	0.36826	0.49849	0.13023	2.82776	200.528
6	B-6 x dist.	0.45519	0.61616	0.16097	2.82779	200.530
	Acid treated					
7	B-6 x dist.	0.45159	0.61128	0.15969	2.82791	200.538
	Acid treated					
8	A-6 x dist.	0.31315	0.42389	0.11074	2.82779	200.530
	Acid treated					
9	A-6 x dist.	0.13656	0.18485	0.04829	2.82791	200.538
	Acid treated					
10	B-6 x dist.	0.23775	0.32183	0.08408	2.82766	200.521
Average of all analyses					2.82781	200.532

ratio as well as the atomic weight of mercury were calculated.

E. RESULTS.

The average result obtained, using this simplified method, gave 200.532 as the atomic weight of mercury which differs with the present value of 200.61 as given by the Third Report of the Committee on Atomic Weights of the International Union of Chemistry.¹⁰

SUMMARY.

1. The synthesis of mercuric chloride by the action of chlorine on mercury is described.
2. The design of a new reaction vessel for this purpose is submitted.
3. The use of this reaction vessel in the determination of a hitherto unused ratio of Hg : 2Cl is described.
4. From the new ratio, as a means of ten analyses, 200.532 is calculated to be the atomic weight of mercury.

